

# An Airborne Smoke Sampling Package for Field Measurements of Fires

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## Abstract

A unique airborne smoke sample package (ASSP) for determining the smoke yield of large fires has been developed. The uncertainty in the average smoke yield at the 95% confidence interval is about  $\pm 7\%$  of the average of three repeat measurements. The ASSP, which weighs less than 4 kg, is light enough to be flown suspended below a tethered helium-filled balloon or attached to a small radio-controlled aircraft. Measurements are made by flying the sampling equipment into a fire's smoke plume. Additional smoke plume measurements that can be made with the ASSP include particle size distribution using a cascade impactor, smoke agglomerate structure using transmission electron microscope (TEM) grids, and polycyclic aromatic hydrocarbons (PAHs) analysis using various sorbent tubes. The application of the ASSP in measuring laboratory and large outdoors petroleum pool fires is discussed. Smoke yield values measured in field burns of Louisiana crude oil range from 0.080 to 0.137, and the primary sphere diameter of the agglomerates is as large as 0.15  $\mu\text{m}$ .

## Introduction

There is a need to characterize the amount and chemical makeup of smoke from large fires to assess the potential air quality and environmental impact. One example of such a fire is the *in situ* burning of crude oil. Evidence based on laboratory studies<sup>1,2</sup> and field studies<sup>3</sup> indicates that it is feasible to ignite and burn a large fraction of crude oil contained in a fire-resistant boom system. However, the environmental impact of such burns needs to be quantified. To do this, measurements of  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{SO}_2$ , smoke particulates, polycyclic aromatic hydrocarbons (PAHs), and unburned oil residue produced by combustion are needed. The smoke plume composition data are needed as input to smoke plume dispersion and particulate deposition computer models, such as the Large Eddy Simulation Model being developed at NIST.<sup>4</sup> These computer models will aid in making decisions about where and when to burn petroleum products that have been released into the environment.

A laboratory study by Benner *et al.*,<sup>5</sup> using a 60 cm diameter pool fire, quantified the yield of particulates and PAH in the smoke, PAH concentration in the original crude, and the post burn residue. Although laboratory-scale fires provide valuable data, there is also a need to make similar measurements at a larger scale anticipated

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Keywords: Airborne sampling, field tests, fire research, fires, measurement, measuring instruments, oils, particulates, pool fires, sampling, smoke, smoke yield.

for use in response to actual spills. One of the challenges associated with larger-scale fires is the sampling of the combustion products for fires with flames as high as 30 m.

This paper focuses on the development and testing of an airborne smoke sampling package (ASSP) for collecting smoke aerosol and combustion gases from the smoke plume produced by field-scale burns. While smoke sampling equipment has been used at ground level<sup>6,7</sup> and by manned aircraft,<sup>8</sup> the ASSP is the first package designed to be carried aloft by a tethered balloon or a remote control aircraft. The performance of the ASSP is evaluated by comparing the results with a standard method in side-by-side sampling from laboratory-scale burns. Results are presented for field-scale burns up to 232 m<sup>2</sup> in fuel area. This paper consists of a description of the equipment, an explanation of the carbon balance method for determining smoke yield, procedures used to measure smoke, results from laboratory and field experiments, and an uncertainty analysis.

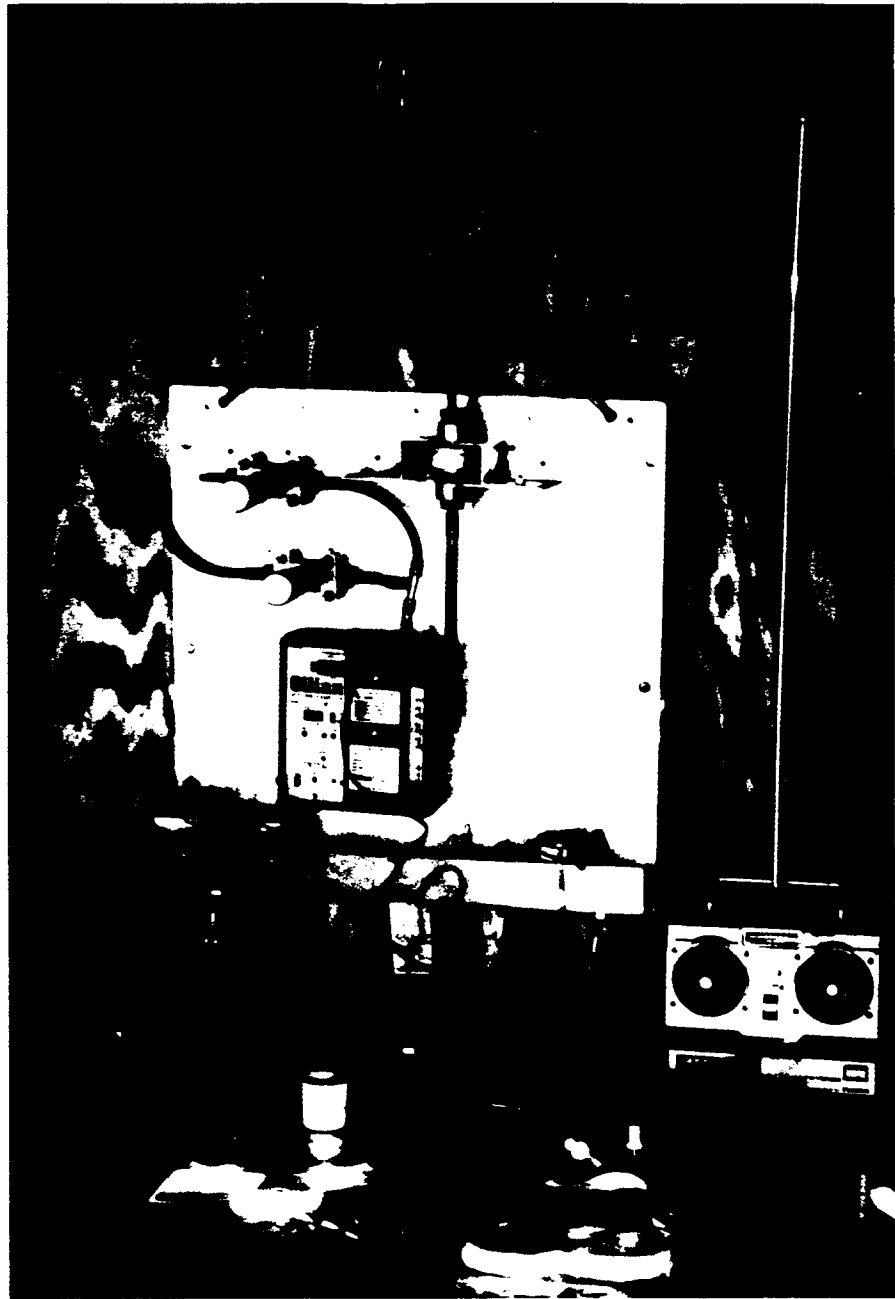
## Experimental Equipment

The development of small, light-weight, battery-powered pumps used for personal environmental air sampling has made it possible to assemble a smoke yield measurement system that is light enough to be flown by a 12 m<sup>3</sup> balloon. The ASSP shown in Figures 1 and 2 consists of a 47 mm diameter aluminum filter holder, a 67 cm<sup>3</sup>/s (4 L/min) constant flow pump (Gillian<sup>9</sup> Model HFS 513A), two micrometer metering valves used to split the sample flow from the exhaust line, and a fabric envelope used to hold a nominal 5 liter polyvinyl fluoride (PVF) plastic sample bag. A similar approach to sampling, including the use of a constant flow pump and gas sampling bag, was used by Ward<sup>6</sup> in sampling biomass fires from a tower. The ASSP's support platform is made of aluminum 0.9 mm (1/32 in) thick with a cross-section of 38 cm by 38 cm. A radio-controlled actuator is attached to the pump to turn the pump on remotely as the ASSP enters the plume and turn it off at the desired time. In addition, this remote control unit activates a strobe light that allows the operator to verify that the sample pump is running. The system's total weight is approximately 3.2 kg. Work is currently in progress to reduce the weight of the system to about 1 kg by using a plastic mounting frame and light-weight plumbing components. In addition, a larger, multi-pump sampling package is being built to take several simultaneous samples/measurements in a smoke plume. The package would be supported by a 40 m<sup>3</sup> balloon or carried suspended on a line below a manned helicopter.

In the present study, the platform was suspended below a blimp-shaped, helium-filled balloon 5.6 m long and 2.3 m diameter. A team of two can position the sampling package to heights of more than 100 m in winds up to about 0.5 m/s (10 to 15 mph).

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<sup>9</sup>Certain materials and equipment are identified in this report to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for the purpose.



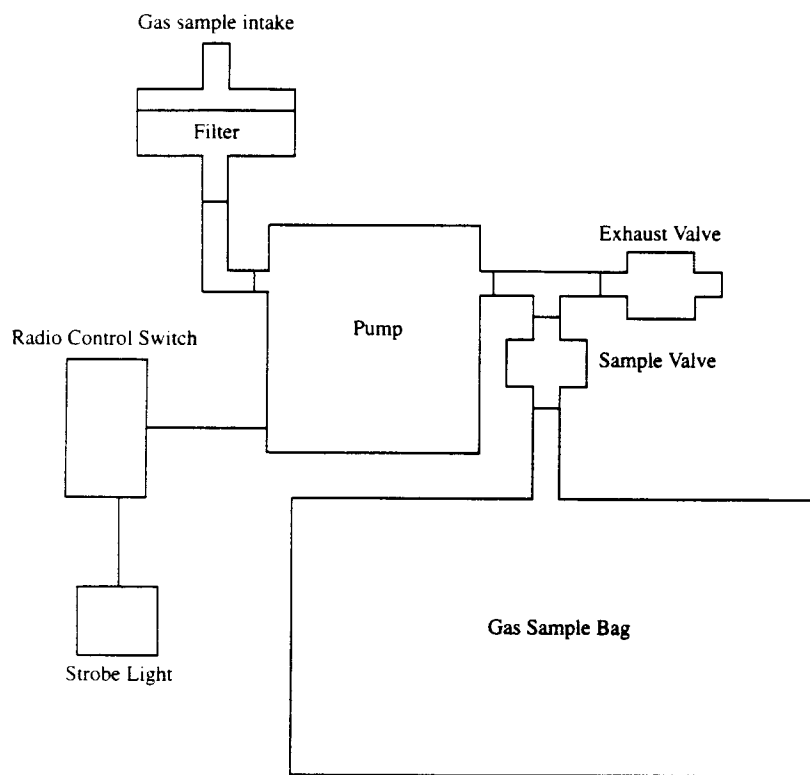
**Figure 1. Assembled smoke sampling package.**

The sampling package is also small enough and light enough to be carried by robust, remotely controlled model helicopters and fixed-wing aircraft.

In addition to the design being used for smoke yield sampling, minor alterations can be made to the ASSP to allow it to measure other smoke properties. By replacing the filter holder with a cascade impactor, the aerodynamic size distribution of the smoke can be measured. By attaching transmission electron microscope (TEM) grids to the support platform, smoke agglomerates may be collected for microscopic study. Toxic products, such as PAHs, can be sampled by adding sorbent tubes to the sampling train. Plume temperatures may also be measured by attaching a thermocouple and recording device.

## Smoke Yield

Smoke yield is defined as the mass of smoke aerosol generated per mass of fuel consumed. The smoke aerosol collected during these experiments contains both solid



**Figure 2. Diagram of smoke sampling package components.**

material (graphitic carbon) and condensible hydrocarbons from the fire plume. Two methods for determining smoke yield are used in this study. The first is the flux method, which measures the smoke collected on a filter and the mass loss from the burning specimen.<sup>1,9</sup> This type of measurement works well in a laboratory test environment where all the products of combustion are collected and drawn through an exhaust stack. The defining equation for smoke yield based on the flux method  $\epsilon_1$  is given by:

$$\epsilon_1 = \left( \frac{m_s}{m_f} \right) \phi \quad (1)$$

where  $m_s$  is the smoke mass collected on the filter from an exhaust stack sample,  $m_f$  is the fuel mass consumed during filter collection, and  $\phi$  is the ratio of mass flow of air up the stack to the mass flow through the sample filter.

The second means of determining smoke yield is referred to as the carbon balance method.<sup>1,6,9</sup> This procedure is unique in that it does not require knowledge of the total gas flow from a fire or its burning rate. Thus, it can be used in the field, as well as in a laboratory. As with the flux method, a smoke sample must be collected on a filter. In addition, a simultaneous plume gas sample must be taken as the smoke is collected. The carbon balance method requires a determination of the ratio of smoke mass collected to the total mass of carbon in the combined smoke/gas sample. This is accomplished by dividing the smoke mass by the sum of the smoke mass and the mass of carbon contained in CO and CO<sub>2</sub> sampled from the smoke plume. Therefore, this procedure uses a partial carbon balance to obtain the smoke yield value. A complete carbon balance would include corrections for additional carbon-containing gases released by the fire. Laboratory studies indicate that, under free burning conditions (open burning), the contribution of such gases is on the order of 2% or less.<sup>10</sup>

The carbon balance method also assumes that the smoke aerosol and the gaseous products of combustion are well mixed. This is expected to be a valid assumption near the fire, provided the aerodynamic diameter of the smoke aerosol is less than 10  $\mu\text{m}$  so that particle sedimentation is insignificant. A 10  $\mu\text{m}$  sphere with unit density will settle 6 cm, which is small compared to a nominal plume diameter of at least 10 m, over a time of 20 seconds, a nominal transit time from the flame to the collection of the smoke.

The following equation is used for calculating smoke yield  $\epsilon_2$  based on carbon balance:

$$\epsilon_2 = \frac{f m_s}{\left[ m_s + 12n_t [X(\text{CO}) + (X(\text{CO}_2)_b)] \right]} \quad (2)$$

where

$$n_i = \frac{PV_s}{RT} \quad (3)$$

The quantity  $f$  is the carbon mass fraction of the fuel (approximately 0.85 for crude oils).  $m_i$  is mass of smoke sample collected on a filter, and the constant 12 represents the molar mass of carbon. The quantities  $X(\text{CO})$  and  $X(\text{CO}_2)$  are the mole fractions of CO and CO<sub>2</sub> of the gas sample taken during the test and  $X(\text{CO}_2)_b$  is the mole fraction of background CO<sub>2</sub> in the air before the test. The quantity  $V_s$  is the volume of gas sampled where  $P$  and  $T$  represent the atmospheric pressure and ambient temperature at the fire site.

### Experimental Procedure for Smoke Yield

The general method used for sampling smoke plumes for either laboratory tests or field tests follows the same basic process. First, the filter must be carefully weighed using a balance with a measurement resolution of at least 0.01 mg. A clean sample filter is placed into the filter holder. The sampling system is leak-tested, and the pump flow is calibrated before each test with an electronic bubble flow meter. The flow was typically adjusted to be 50 to 75 cm<sup>3</sup>/s (3 to 4.5 L/min). The gas sample flow to the PVF bag is adjusted to provide a constant flow into the sample bag throughout the test. Back pressure from the bag must not change the flow into the bag or the fraction of gas sampled will vary with test time, providing an invalid gas sample. In the work reported here, sample bags were generally only filled to about 25 to 50% of their capacity. Flow to the bag will vary from test to test, depending upon the sampling time.

After the calibration is completed, a filter weighed with a 0.01 mg sensitivity microbalance is placed in the filter holder. A gas sample bag is attached to the gas sample port and placed in the support pocket on the sampling platform. A check is made of the radio-control switching system, and the sampling platform is attached to the balloon tether line. This sampling package is sent aloft to collect a clear air sample which provides data on the background gas concentrations. Following collection of the background gas and particulate samples, the filter and gas sampling bag are replaced. After the fire is started, the package is sent aloft. When the package enters the smoke plume, the sampling pump is started by radio control, and a stopwatch is started. The sample package is kept in the smoke plume for the predetermined time and is then removed. As the sampling system leaves the plume, the pump is turned off, and the total sampling time is recorded. When the system is retrieved, the gas sample bag valve is closed, and the fire test sample and background sample are prepared for analysis by a gas chromatograph. The primary gases measured are N<sub>2</sub>, O<sub>2</sub>, CO, and CO<sub>2</sub>. The particulate filter is carefully removed to avoid contamination or any loss of smoke. It is then weighed to determine the mass of smoke particulate collected. Finally, smoke yield is calculated using Equation (2).

**TABLE 1**  
**Comparison of Flux Method to Carbon Balance Field Method**

Test	Flux Method	Carbon Balance Field System
1	0.129	0.145
2	0.115	0.133
3	0.130	0.144
Average	0.125	0.141
$\sigma$	$\pm 0.008$	$\pm 0.007$

### Results from Laboratory and Field Tests

Two identical ASSPs, as described above, have been laboratory-tested to determine their ability to sample smoke and gases from fire plumes and provide accurate smoke yield values. Results are also provided from field applications.

### Laboratory Experiments

Initial testing of the ASSPs involved the comparison of these units to a calibrated flux method smoke yield system designed by Mulholland, *et al.*<sup>1,9</sup> The facility at NIST collects all smoke and gases from fires, up to about 400 kW, in a hood, with a known fraction of the total flow passing through a filter. During the filter collection process, the fuel's mass loss is measured. The testing involved fuel oil pool fires with a 40 cm diameter pan. A layer of oil 1 cm thick was floated on water. The burning rate of the fuel increased for about 60 seconds, was steady for about 400 seconds, and, just before flame extinction, increased greatly for 10 to 20 seconds during boilover. The heat release rate from the fires was about 100 kW. The smoke collection was started in each case 1 minute after ignition and continued for 5 minutes during the steady burning phase. It is important to collect over the same time period, since the smoke yield increases on the order of 10 to 20% with time during the steady burning phase.<sup>1</sup>

The ASSP probe was located in the 50 cm diameter exhaust stack at the same height as the fixed laboratory system and within 5 cm laterally. Both sampling systems were operated with flows and probe opening diameters that would provide equivalent face velocities, and both systems sampled for the same time period. As can be seen from the results in Table 1, the field system's average value is within 13% of the average of results obtained by the laboratory flux method. Below, we describe additional measurements to assess the uncertainty in the ASSP measurement and present a quantitative uncertainty analysis.

The carbon balance method for measuring smoke yield requires that a known volume of sample be drawn from a fire plume. This is accomplished with the ASSP using a pump with a constant sampling flow rate. To quantify the pump's constant flow characteristics as the filter is loaded with smoke, the pump flow was monitored before and after collecting 6 mg of smoke on the filter, which is about 5 times the normal loading. The flow decreased by only 0.6% from 66.7 cm<sup>3</sup>/s (4.00 L/min) to 66.3 cm<sup>3</sup>/s (3.98 L/min), thus verifying the effectiveness of the pump's flow controller for maintaining constant flow as the smoke collected on the filter.

During several of the field tests described in the next section of this report, a thermocouple was flown with the smoke yield package. Smoke plume temperatures at the sample point were consistently found to be between 30° to 40°C. As a result of this finding, an experiment was carried out to determine the influence of temperature on the pump flows since the total mass flow is critical in the calculation of smoke yield.

The experiment was designed to evaluate pump flows at room temperature and at temperatures equivalent to those found in the fire plume. Tests of pump performance were carried out at 23°, 30°, 40°, 50°, and 60°C. In these experiments, a pump was pre-calibrated at room temperature—23°C—and found to have a flow of 73.9 cm<sup>3</sup>/s (4.4 L/min) using an electronic bubble flow meter. The pump, while still operating on its internal battery, was then placed inside a 1 m<sup>3</sup> volume heated chamber and connected to a calibrated dry test meter on the outside of the chamber with a piece of coiled copper tubing 1.2 m long. Copper tubing was used to reduce gas temperature from the heated chamber to room conditions before it reached the dry test meter. If the pump behaved ideally with constant mass flow independent of chamber temperature, the dry test meter readings would also be independent of the chamber temperature. Two ports 1 cm in diameter allowed makeup air to flow into one side of the chamber as heated air was removed from the other side by the pump. A thermocouple was placed at the pump inlet to measure air temperature entering the pump. Each of the elevated temperature tests was conducted consecutively. The chamber temperature was increased between runs; time was allowed for the chamber and pump to equilibrate before the next series of flow measurements were made. This series of tests lasted about 120 minutes.

Results from this experiment are shown in Table 2. As can be seen, the pump flows varied about 4% from 75.1 cm<sup>3</sup>/s at 30°C to 72.1 cm<sup>3</sup>/s at 60°C. If the pump performed at constant volumetric flow rather than constant mass flow, the predicted flow change for the flow meter maintained at ambient conditions would have been a 10% decrease. So it is seen that the pump partially compensates for the changing temperature. The slight dependence of flow on temperature is included in the uncertainty analysis below.

After laboratory evaluation, the smoke yield system was used to measure smoke yield from three different crude oils: Alaskan North Slope, Alberta Sweet, and Arabian/Murban crude. Experiments were conducted at four different pool diameters: 0.4 m, 0.6 m, 1.0 m, and 3.0 m.<sup>10</sup> The 0.4 m and 0.6 m laboratory tests were carried out at NIST where the smoke yield system drew samples from the test exhaust duct. The 1.0 m and 3.0 m indoor fires were conducted at the Fire Research Institute in



**TABLE 2**  
**Characterization of Sampling Pump**

Characterization of Sampling Pump at Room Temperature (23°C) Using a Bubble Flow Meter		
	Flow (cm <sup>3</sup> /s)	
	74.5	
	73.9	
	73.7	
	73.6	
	74.4	
	75.3	
	72.9	
	73.5	
	73.6	
	73.4	
Average	73.9	(4.43 L/min)
O	0.7	

Characterization of Sampling Pump at Elevated Temperature	
Inlet Temperature (°C)	Flow (cm <sup>3</sup> /s)
30	75.1
40	74.4
50	72.1
60	72.1

Tokyo, Japan. Samples were taken while the smoke yield system was suspended in the smoke plume or in the smoke layer created by the crude oil fire experiment.<sup>9,10</sup> Results from these tests are presented in Figure 3.

### Uncertainty Analysis

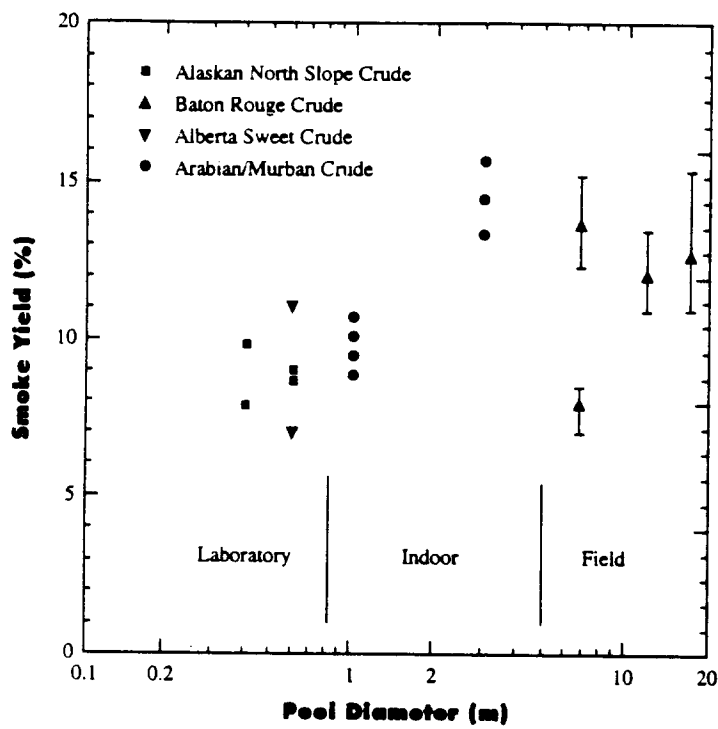
The determination of uncertainty in  $\epsilon_2$  requires estimates of experimental imprecision and the systematic uncertainties associated with the  $m_s$ ,  $n_r$ ,  $X(\text{CO}_2)$ , and  $X(\text{CO})$ . The systematic uncertainties can be estimated by computing the logarithmic derivative,

$\partial(\ln \epsilon_2) / \partial p_i$ , where the parameter  $p_i$  represents  $m_s$ ,  $n_i$ , and so on. Following this procedure, we obtain the following estimates for the individual uncertainties:

$$\frac{u_m}{\epsilon_2} \approx \frac{\delta m_s}{m_s} \quad (4)$$

$$\frac{u_{n_i}}{\epsilon_2} \approx \frac{\delta n_i}{n_i} \quad (5)$$

$$\frac{u_{co_2}}{\epsilon_2} \approx \frac{\delta X_{co_2}}{X_{co_2} - X_{co_2,b}} \quad (6)$$



**Figure 3. Smoke yield percent vs. pool diameter.**

$$\frac{u_{co}}{\epsilon_2} \approx \frac{\delta X_{co}}{X_{co_2} - X_{co_2,b}} \quad (7)$$

The  $\delta$  refers to the uncertainty in a specific parameter; for example,  $\delta m_s$  is equal to  $\pm 0.01$  mg. These estimates are based on the approximations that most of the carbon produced by the flame is in the form of  $CO_2$  and that the systematic uncertainty in both  $CO_2$  measurements, sample  $CO_2$  and background  $CO_2$  will be similar in magnitude and in the same direction. That is, both readings will be low or high relative to the exact value for the plume reading and the background reading.

There are several contributions to the uncertainty in  $n_t$ ,  $\delta n_t$ . The most significant factor affecting  $\delta n_t$  is the thermal effect, which corresponds to a change in the pump flow rate with a change in the temperature. For temperatures in the range  $20^\circ$  to  $45^\circ C$ , the flow uncertainty is estimated from Table 2 to be  $\pm 1.5$  cm<sup>3</sup>/s at a nominal flow of 74 cm<sup>3</sup>/s. This corresponds to  $\delta n_{t(temp)}/n_t = 0.020$ . There is a slight effect of filter loading on the flow as discussed above, and this corresponds to  $\delta n_{t(load)}/n_t = 0.006$ .

The imprecision in flow calibration expressed as the standard error  $\sigma/n^{1/2}$  for three replicate measurements is 0.39 cm<sup>3</sup>/s, based on the data in Table 2. The corresponding uncertainty is given by  $dn_{t(i)}/n_t = 0.005$ . The combined error in  $n_t$  is obtained by adding in quadrature the imprecision to 1/3 the sum of the systematic errors.

$$\delta n_t = \left[ \delta n_t^2 + 1/3 (\delta n_{t(temp)} + \delta n_{t(load)}) \right]^{1/2} \quad (8)$$

From Equations (5) and (8), we obtain  $u_{n_t}/\epsilon_2 = \pm 0.013$ . Uncertainties in the pressure reading and in the accuracy of the flow calibration were at least a factor of 5 smaller than the combined uncertainty and were not included.

We estimate the other uncertainties based on the laboratory-scale tests summarized in Table 2. From the accuracy of the micro balance—0.01 mg—and a nominal filter loading of 2 mg, we obtain  $u_m/\epsilon_2 = \pm 0.005$ . Based on concentrations of 0.15%  $CO_2$  in the stack and 0.035%  $CO_2$  ambient and an uncertainty of 0.001% in the  $CO_2$  measurement, we obtain  $u_{co_2}/\epsilon_2 = \pm 0.009$ . No CO was detected using the GC analysis of the bag samples. An independent measurement of the CO in the stack with a non-dispersive infrared analyzer indicated a ratio of CO to  $CO_2$  background corrected concentrations of about -0.040. We note that this uncertainty,  $u_{co}/\epsilon_2$ , is one-sided. Using the value of  $\sigma$  given in Table 1, we compute the imprecision component of uncertainty using the following formula:

$$\frac{u_i}{\epsilon_2} = \frac{\pm \sigma}{\epsilon_2 \sqrt{n}} = \frac{\pm 0.007}{0.141\sqrt{3}} \quad (9)$$

The result is  $u_i/\epsilon_2 = \pm 0.029$ .

Now we can compute the combined uncertainty,  $u_c$ , using an analog of Equation (8).

$$u_c = \left[ u_i^2 + 1/3(u_m^2 + u_{n_i}^2 + u_{co_2}^2 + u_{co}^2) \right]^{1/2} \quad (10)$$

We obtain  $u_c/\epsilon_2 = \pm 0.031 / -0.038$ . The imprecision is the major component of the total uncertainty. We obtain an expanded uncertainty  $U/\epsilon_2 = \pm 0.062 / -0.076$  corresponding to 95% confidence intervals by multiplying  $u_c$  by a factor of two. The confidence interval in terms of  $\epsilon_2$  is given by  $0.130 \leq \epsilon_2 \leq 0.150$ .

The expanded uncertainty of the average smoke yield obtained by the ASSP overlaps with the one sigma spread of the data from the flux method. We suspect that there is a systematic uncertainty in the flux method, such as a drift in the stack flow meter, resulting in a low value of  $\epsilon_2$ . This suspicion is based on an independent determination of  $\epsilon_2$  of 0.151 based on CO and CO<sub>2</sub> results from the nondispersive infrared analyzers used in sampling the stack gases.

For the field data, less smoke is collected, and the CO<sub>2</sub> concentration is lower. For a typical case with a filter collection of 0.5 mg and a plume CO<sub>2</sub> reading of 0.060% and  $\epsilon_2$  equal 0.141, we compute based on Equation (8) the 95% confidence interval  $0.124 \leq \epsilon_2 \leq 0.157$ . In this case, the imprecision  $u_i$  equals  $\sigma$ , since only a single measurement is made. Again, the imprecision is the major factor in the uncertainty analysis, and this could be reduced by performing several repeat measurements.

It should be noted that this uncertainty analysis is for the ASSP only and does not include the variability of the smoke yield with time as the oil burns or possible environmental effects on smoke yield, such as the wind velocity.

### Results of Field Experiments

The smoke yield sampling system described in this report has been used to measure smoke emitted from Louisiana crude oil fires at the U.S. Coast Guard Fire and Safety Test Detachment in Mobile, Alabama. These fires ranged in effective burn diameter from 6.88 to 17.2 m. The effective burn diameter is the diameter of a circle with the same area as the square burn pans. As can be seen from Table 3 and Figure 3,  $\epsilon_2$  ranges from 0.080 to 0.137 for the four tests. The uncertainty bars bracketing the field measurement data in Figure 3 were calculated with Equation (10) and using the measured values of  $m_i$  and volume concentrations of CO<sub>2</sub> given in Table 3.

Figure 4 shows the flames and smoke during one of the experiments in Mobile. A full description of the tests referenced here is beyond the scope of this report and has been published in a separate report,<sup>4</sup> which focuses on the field scale results. Table 3 was prepared to provide information on actual measured results for the field tests. As can be seen in the table, data values for CO<sub>2</sub> vary from 530 ppm to 650 ppm. This is primarily caused by the sampling location—that is, the height of the ASSP and what fraction of time the ASSP is in the smoke plume. Typically in these experiments, the ASSP was flown from 50 to 150 m beyond the test fire's flame tip. These CO<sub>2</sub> concentrations are about twice the ambient value, the CO concentration is below a

**TABLE 3**  
**Smoke Yield Field Data**

Test	Burn Area (m <sup>2</sup> )	Gas Sample Volume (L)	CO <sub>2</sub> Concentration (ppm)		CO Concentration (ppm)		Smoke Mass (mg)	Smoke Yield
			plume	background	plume	background		
1	37.2	20.8	600	390	trace	0	0.41	0.137
2	37.2	56.6	650	380	trace	0	0.75	0.080
3	114.0	61.2	630	370	trace	0	1.29	0.121
4	181.0	77.5	530	420	trace	0	0.73	0.127

Note: The above tests were conducted using Louisiana crude oil at the U.S. Coast Guard Fire and Safety Test Detachment in Mobile, Alabama.



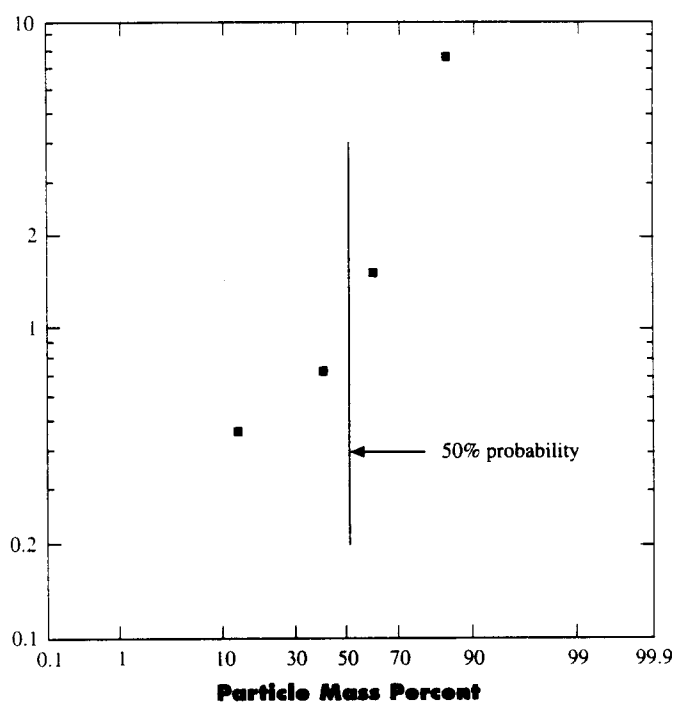
**Figure 4. U.S.C.G. Fire and Safety Test Detachment burn facility in Mobile, Alabama.**

detectable limit of the GC, and the mass concentration of particulate—10 to 20 mg/m<sup>3</sup>—is hundreds of times greater than the ambient particle concentration.

### Particle Size Distribution

In addition to collecting smoke and gases to determine smoke yield, the portable sampler can be used to characterize the size distribution and chemical makeup of the smoke. Figure 5 shows a typical particle size distribution, and Figure 6 is a transmission electron microscope photo of smoke agglomerates taken from Louisiana crude oil fire tests at Mobile.

The particle size distribution was obtained by connecting a cascade impactor (Marple Impactor Model 298, Graseby Andersen Co.) to the smoke yield package where the particulate filter would normally be located. The smoke agglomerates collection was passive: a transmission electron microscope grid 3 mm in diameter was attached to the smoke yield platform with double-sided tape. Some of the smoke particles in the plume were deposited on the grid as a result of Brownian motion and thermophoresis, which results from the surface temperature of the collection assembly



**Figure 5. Particle diameter vs. particle mass percent as sampled by a cascade impactor.**

being lower than the plume temperature. On the plot in Figure 5, note that with this oil, particles smaller than  $1\text{ }\mu\text{m}$  make up about 50% of the smoke collected. In addition, about 90% by mass of the smoke aerosol has an aerodynamic diameter less than  $10\text{ }\mu\text{m}$ , indicating that particle sedimentation will not significantly affect the uniform mixing of the smoke aerosol and the  $\text{CO}_2$  at the collection point.

The electron microscope photograph shows that the oil from field-sized fires produces two general spherule particle sizes which make up the agglomerates. The larger spherule sizes are on the order of  $0.15\text{ }\mu\text{m}$ , and the smaller spheres are about  $0.060\text{ }\mu\text{m}$ . This larger spherule size was also found in both a 3.1 m indoor fire test in Japan and in a large-scale aviation fuel pool fire.<sup>11</sup> Previous laboratory-scale experiments ranging in size from a burner 1 cm in diameter to a 60 cm pool burn indicated primary particle size in the range of 0.02 to  $0.05\text{ }\mu\text{m}$ .

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**Figure 6. Transmission electron microscope photograph of Baton Rouge crude smoke agglomerates from a field experiment.**



### PAH Analysis

A modified version of this sampling package was used in Kuwait to collect PAH in both the gas and particulate phase. A specially designed filter holder was used, followed by a sorbent tube. Twenty minutes of sampling from the whitish ground-level smoke plume from an oil well fire resulted in the collection of about 1 mg of smoke, which was adequate for GC-MS analysis of 13 PAHs, including benzo[a]pyrene.

### Summary and Conclusions

A unique airborne smoke sampling package (ASSP) has been developed that can provide accurate information on the smoke particulate yield based on the carbon balance method. From a laboratory study, the estimated 95% confidence limits for a mean smoke yield of 0.141 are  $0.130 \leq \epsilon_p \leq 0.150$ . By performing replicate field measurements and by improving the CO and CO<sub>2</sub> measurements, the 95% confidence interval for field measurements could approach the laboratory value.

Field-scale measurements with burn areas up to 232 m<sup>2</sup> have been successfully performed by attaching the sampling package to a 12 m<sup>3</sup>, helium-filled, blimp-shaped balloon. The sampling system has been lofted up to 150 m with wind velocities up to 0.5 m/s with two people controlling the position of the ASSP in the plume. It has also been demonstrated in field tests that the particle size distribution can be obtained with a cascade impactor, agglomerate structure can be determined by collecting samples on electron microscope grids, and PAH for both the gaseous phase and particulate can be sampled for measurement. Preliminary results suggest that there are scale effects in terms of an increased smoke yield and increased primary particle size of the smoke agglomerates for large fires. However, more study is needed to determine the generality of these preliminary observations.

In addition to studying smoke production from burning crude oil, the ASSP system could be applied to both planned and accidental fires and to other hazardous gaseous/particulate releases. Our experience has shown that, for smoke plumes emanating from an individual fire, the ability to position an ASSP in the high concentration plume for an extended period offers better sampling capability than that of either radio-controlled or manned aircraft. The aircraft are kept from flying into a high-concentration plume near the source by poor visibility, intense turbulence, and the potentially damaging impact of the plume on the aircraft's engines. Aircraft were used for smoke sampling far down wind of the Kuwait oil well fires.<sup>12</sup> However, only limited near-plume data were obtained because of the difficulties described above.

### Acknowledgments

Ed Tennyson served as scientific officer for the Mineral Management Service (U.S. Department of Interior) for this project. Dr. David Evans was the Project Leader and Mr. Doug Walton was the Test Program Technical Director.

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